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[Title of the Invention]

METHOD FOR PRODUCING NONAQUEOUS ELECTROLYTE BATTERY AND POSITIVE
ACTIVE MATERIAL

[Abstract]

[Problem to be Solved]

A nonaqueous electrolyte rechargeable battery with high capacity
and superior cycle property is provided.

[Solution]

The present invention uses as a positive electrode active material $\text{LiNi}_x\text{M}_{1-x}\text{O}_2$ (M is one or more selected from Co, Mn, Cr, Fe, V, and Al, $x: 1 > x \geq 0.5$), regulates the particle size and shape of the microcrystal particle microcrystal particles of the active material and the aggregated particles which are microcrystal particle microcrystal particles aggregated together, and uses a positive electrode plate which uses a mixture of these particles.

[Claims for the Patent]

[Claim 1]

A nonaqueous electrolyte battery comprising a negative electrode plate, a positive electrode plate having as a positive active material $\text{LiNi}_x\text{M}_{1-x}\text{O}_2$ (M is any one or more of Co, Mn, Cr, Fe, V, and Al, $x: 1 > x \geq 0.5$), and a separator that is interposed between said negative and positive electrode plates, wherein said positive active material is composed of a mixture of a microcrystal particle microcrystal particle having a Feret diameter as determined by SEM observation is in the range of 0.1 to 2 μm and an aggregated particle having a Feret diameter in the range of 2 to 20 μm that is a multiple of said microcrystal particle microcrystal particles aggregated together.

[Claim 2]

The nonaqueous electrolyte battery according to claim 1, wherein the aggregated particle has a shape of a sphere or an oval sphere.

[Claim 3]

The nonaqueous electrolyte battery according to claim 1, wherein the blend ratio of the microcrystal particle microcrystal particles

relative to the aggregated particles is in the range of 5 to 50% in ratio by weight.

[Claim 4]

The nonaqueous electrolyte battery according to claim 1, wherein the microcrystal particle is a ground aggregated particle.

[Claim 5]

A method for producing a positive active material for a nonaqueous electrolyte battery, wherein the positive active material is $\text{LiNi}_x\text{M}_{1-x}\text{O}_2$ (M is one or more selected from Co, Mn, Cr, Fe, V, and Al, $x: 1 > x \geq 0.5$), comprising blending an aggregated particle which is multiple microcrystal particles having a Feret diameter as determined by SEM observation of 0.1 to 2 μm that are aggregated together, wherein the aggregated particle is $\text{LiNi}_x\text{M}_{1-x}\text{O}_2$ (M is one or more selected from Co, Mn, Cr, Fe, V, and Al, $x: 1 > x \geq 0.5$) having a Feret diameter in the range of 2 to 20 μm , with lithium carbonate or lithium hydroxide; and performing a heating process of this mixture to obtain the positive active material.

[Claim 6]

The method for producing a positive active material for a nonaqueous electrolyte battery according to claim 5, wherein the aggregated particle has a shape of a sphere or an oval sphere.

[Claim 7]

A method of producing a positive active material for a nonaqueous electrolyte battery, wherein the positive active material is $\text{LiNi}_x\text{M}_{1-x}\text{O}_2$ (M is one or more selected from Co, Mn, Cr, Fe, V, and Al, $x: 1 > x \geq 0.5$), comprising grinding a part of the aggregated particle represented by $\text{Ni}_x\text{M}_{1-x}(\text{OH})_2$ (M is one or more selected from Co, Mn,

Cr, Fe, V, and Al, $x: 1 > x \geq 0.5$) and having a Feret diameter as determined by SEM observation in the range of 2 to 20 μm , wherein the aggregated particle is multiple microcrystal particlemicrocrystal particles having a Feret diameter as determined by SEM observation of 0.1 to 2 μm that are aggregated together, until the particles are reduced to said microcrystal particlemicrocrystal particles; blending this ground material with said aggregated particle in an ungrounded state; and then blending the mixture with lithium carbonate or lithium hydroxide; and performing a heat treatment of these mixtures to obtain the positive active material.

[Claim 8]

The method for producing a positive active material for a nonaqueous electrolyte battery according to claim 7, wherein the blend ratio of the ground aggregated particle relative to the ungrounded aggregated particle is in the range of 5 to 50% in ratio by weight.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a nonaqueous electrolyte rechargeable battery and a method of producing a positive active material thereof, in particular to an improvement of the battery property thereof.

[0002]

[Conventional Art]

In recent years, progression on making consumer electronics portable and cordless has been rapid. Although a nickel cadmium battery or a closed mold small lead accumulator is currently bearing the role as a power source for driving these electronic equipments, high energy

density and reduction of size and weight for the rechargeable batteries used as the power source for driving electronic equipments have become strong as the demand for portable and cordless consumer electronics have progressed and established.

[0003]

Moreover, these batteries have in recent years been noted as a power source for cellular phones, and with the rapid expansion of commercial scenes, the desire for prolonged call duration and improvement of cycle life has been very intense.

[0004]

In such circumstances, a nonaqueous electrolyte rechargeable battery has been proposed, wherein the battery uses as a positive active material a lithium transition metal complex oxide which shows high charge and discharge voltage, for example LiCoO_2 (for example, Japanese Patent Laid-Open No. 63-59507), LiNiO_2 , which furthermore aims at high capacity (for example U.S. Pat. No. 4302518), and a complex oxide of multiple metal elements and lithium (for example $\text{Li}_y\text{Ni}_x\text{Co}_{1-x}\text{O}_2$: Japanese Patent Laid-Open No. 63-299056 and $\text{Li}_x\text{M}_y\text{N}_z\text{O}_2$ (wherein M is at least one selected from Fe, Co, and Ni, and N is at least one selected from Ti, V, Cr, and Mn): Japanese Patent Laid-Open No. 43-267053); and wherein the battery utilizes insertion and extraction of a lithium ion.

[0005]

Moreover, methods for improving the physical properties of the positive active material, for example the average particle size (Japanese Patent Laid-Open No. 1-304664, Japanese Patent Laid-Open No. 6-243897, Japanese Patent Laid-Open No. 6-290783, and Japanese Patent Laid-Open No. 7-114942) and shape (Japanese Patent Laid-Open

No. 6-267539 and Japanese Patent Laid-Open No. 7-37576), have been proposed.

[0006]

[Problems to be Solved by the Invention]

However, in a nonaqueous electrolyte rechargeable battery that uses previously reported LiNiO_2 as the positive active material, a problem of cycle deterioration became apparent, wherein the discharge capacity of the battery gradually decreases by repeating charge and discharge cycles.

[0007]

As a result of the present inventors' through investigations, it was found that such deterioration of the properties were due to the following causes.

[0008]

When cycle deteriorated battery was disassembled and an X-ray analysis of the electrode plate was carried out, it was found that in a positive electrode plate which was subjected to repeated charge and discharge cycles, the crystal structure of the positive active material was remarkably changed.

[0009]

It has been reported that with LiNiO_2 , the lattice constant changes in association with charge and discharge of the battery (S. Yamada, M. Fujiwara and M. Kanda, J. Power Source, 54, 209 (1995)), and expansion and contraction is large in both a-axis and c-axis.

[0010]

Thus, it was found that deterioration was caused due to the active material expanding and contracting by repeating charge and discharge cycles, resulting in amorphization of the crystal structure,

micronization of the particle, and detachment of the active material from the electrode plate, which reduces the amount of the active material which can participate in charge and discharge.

[0011]

To oppose such a problem, by using a lithium-comprising complex metal oxide wherein a part of Ni was substituted by another metal, alteration of the crystal structure was reduced and good cycle property was observed.

[0012]

However, although such an active material in which a part of Ni is substituted with another metal element showed improved cycle property, the discharge capacity decreases and the discharge voltage is reduced as well, and there was a problem that the discharge capacity decreases remarkably especially during a high rate discharge in which a high current is passed.

[0013]

Moreover, when micronization of the active material was investigated to improve high rate discharge property, there was a problem that the packing property on the battery electrode plate is remarkably reduced, and the battery capacity itself decreases.

[0014]

The object of the present invention is to solve the problems above related to the conventional positive electrodes, to provide a better positive active material, and to provide a nonaqueous electrolyte rechargeable battery having superior charge and discharge properties by using a particular particle size, particle shape, and packing method for the positive active material.

[0015]

[Means for Solving the Problems]

In order to solve such problems, the present inventors substituted a part of Ni of LiNiO_2 with another metal element, and further made intensive investigations on the size and shape of the particle of the positive active material, as well as the method for packing the active material upon configuration of the electrode plate. Consequently, by controlling these factors, a battery with high capacity as well as good cycle and high rate discharge properties was obtained.

[0016]

In particular, the present invention uses as the positive active material $\text{LiNi}_x\text{M}_{1-x}\text{O}_2$ (M is any one or more of Co, Mn, Cr, Fe, V, and Al, $x: 1 > x \geq 0.5$), wherein the positive active material is a mixture of microcrystal particles having a Feret diameter as determined by SEM observation is in the range of 0.1 to 2 μm and aggregated particles having a Feret diameter of multiple microcrystal particles aggregated together is in the range of 2 to 20 μm .

[0017]

The aggregated particle is desirably a spherical or an oval spherical, and the blend ratio of the microcrystal particles to be blended is desirably in the range of 5 to 50% (ratio by weight).

[0018]

The active material for such spheres can be obtained by blending as raw materials $\text{Ni}_x\text{M}_{1-x}(\text{OH})_2$ (M is any one or more of Co, Mn, Cr, Fe, V, and Al, $x: 1 > x \geq 0.5$) having a Feret diameter as determined by SEM observation that having a Feret diameter of 0.1 to 2 μm in the range of 2 to 20 μm is multiple microcrystal particles aggregated

together, with a lithium salt (either lithium carbonate or lithium hydroxide), and then performing a heat treatment of this mixture.

[0019]

Moreover, the microcrystal particles to be blended can also be obtained by grinding the synthesized positive active material $\text{LiNi}_x\text{M}_{1-x}\text{O}_2$ (M is any one or more of Co, Mn, Cr, Fe, V, and Al, $x: 1 > x \geq 0.5$), or blending the pre-ground raw material $\text{Ni}_x\text{M}_{1-x}(\text{OH})_2$ (M is any one or more of Co, Mn, Cr, Fe, V, and Al, $x: 1 > x \geq 0.5$) with the aggregated particles, and then blending with a lithium salt (either lithium carbonate or lithium hydroxide) and performing a heat treatment of this mixture.

[0020]

In addition, as the method for measuring the particle size, employed is the Feret diameter as determined by SEM observation. This is determined by reading the diameters of particles faced to various directions in a SEM photograph from a certain direction, and then employing the average. (Reference: Basics of Powder Technology (Funtai Kougaku No Kiso), p. 285 (The Nikkan Kogyo Shimbun, Ltd. ed.))

[0021]

[Embodiment of the Invention]

When the positive active material of the present invention is used, it is possible to increase the contact area of the positive active material particle and the electrolyte using a positive active material having as the primary particle a very small microcrystal particle with a Feret diameter as determined by SEM observation of 0.1 to 2 μm , to improve reduction in the interface concentration of the Li ion which causes increased polarization during high rate discharge; and by blending the aggregated particles and the

microcrystal particles, microcrystal particles are packed in the space produced between the aggregated particles, and it is possible to improve electric conductivity between the particles and to remarkably improve the packing property of the active material on the electrode plate.
[0022]

The conceptual diagram of the positive active material of the present invention is shown in Figure 1. By using the method of the present invention, for example by using a laser particle size distribution meter to measure the positive active material of the present invention, it can be seen that the particle size distribution has two peaks.

[0023]

Needless to say, the particle with the larger particle size of the two peaks is the particle size of the aggregated particles, and the peak with the smaller particle size is the particle size of the microcrystal particles added.

[0024]

Such effects cannot be obtained merely by limiting the shape and particle size of the active material, as in for example Japanese Patent Laid-Open No. 6-267539, Japanese Patent Laid-Open No. 1-304664, Japanese Patent Laid-Open No. 6-243897, and Japanese Patent Laid-Open No. 7-37576.

[0025]

[Example 1]

The Examples of the present invention will now be described with reference to the Figures.

[0026]

Figure 2 shows the drawing of longitudinal section of the cylindrical battery used in Example 1. In Figure 2, 1 represents a battery case which is a processed stainless steel plate with organic electrolyte resistance, 2 represents a sealing plate with a relief valve, and 3 represents an insulating packing. 4 represents an electrode assembly, and positive electrode plate 5 and negative electrode plate 6 are wound in a spiral multiple times intermediated by a separator 7, and contained in the case. A positive electrode aluminum lead 5a is pulled out from the above positive electrode plate 5 and connected to the sealing plate 2, and a negative electrode nickel lead 6a is pulled out from the negative electrode plate 6 and connected to the bottom of the battery case 1. 8 is an insulating ring provided on each of top and bottom of the electrode assembly 4.

[0027]

The negative electrode plate 6 and the electrolytes etc. will now be described in detail. For the negative electrode plate 6, 100 parts by weight of carbon powder which was heated coke was blended with styrene-butadiene rubber binder, suspended in aqueous carboxymethylcellulose solution to obtain a paste. This paste was coated on the surface of a copper foil with a thickness of 0.015 mm, and after drying, a negative electrode plate with a thickness of 0.2 mm, width of 37 mm, and length of 300 mm was produced.

[0028]

The method for synthesizing the positive active material will now be described in detail. Nickel sulfate, cobalt sulfate, and sodium hydroxide solution were used. Nickel sulfate and cobalt sulfate solutions were introduced into a container at a constant flow rate, and sodium hydroxide solution was added with sufficient stirring.

[0029]

Nickel cobalt complex hydroxide with various particle sizes was obtained by altering the amount of sodium hydroxide added.

[0030]

The precipitate produced was washed with water, dried, and nickel cobalt complex hydroxide with various particle sizes was obtained.

[0031]

The chemical composition of all the nickel cobalt complex hydroxides obtained was $\text{Ni}_{0.85}\text{Co}_{0.15}(\text{OH})_2$.

[0032]

The nickel cobalt complex hydroxide produced according to the method of this Example was a spherical aggregated particle wherein multiple microcrystal particles (primary particles) in the range of 0.1 to 2 μm were aggregated together, and the Feret diameter of the aggregated particle was 0.5, 2.0, 5.0, 10, 20, and 30 μm each, as determined by measurement of the Feret diameter from a SEM photograph.

[0033]

The nickel cobalt complex hydroxide obtained was blended with lithium hydroxide, calcinated at 700°C for 10 hours under oxidative atmosphere to synthesize $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$.

[0034]

The SEM photograph of the lithium nickel cobalt complex oxide obtained is shown in Figure 3. The lithium nickel cobalt complex oxide synthesized was obtained as spherical aggregated particles having a Feret diameters of 0.51, 2.53, 5.04, 10.1, 20.7, and 30.5 μm each, wherein the aggregated particles were multiple microcrystal particles having a Feret diameters as determined by SEM observation in the range of 0.1 to 2 μm that were aggregated together. The shape of the raw

material nickel cobalt complex hydroxide was mostly maintained, lithium was internally diffused without any alteration in the shape of nickel cobalt complex hydroxide during synthesis, and the reaction was confirmed as progressing.

[0035]

From the lithium nickel cobalt complex oxide obtained by the above synthetic method, 0, 5, 20, 50, 70, and 100% by weight each was extracted, each was ground with a ball mill until reduced into primary particles, and then blended with the ungrounded material.

[0036]

A total of 36 positive active materials were synthesized from the above method. The method for producing a positive electrode plate will now be described.

[0037]

For the positive electrode plate, to 100 parts by weight of the positive active material powdered $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$, 3 parts by weight of acetylene black and 5 parts by weight of fluororesin binder were blended, suspended in N-methylpyrrolidone solution to obtain a paste. This paste was coated on both sides of an aluminum foil with a thickness of 0.020 mm, and after drying, positive electrode plate 5 with a thickness of 0.130 mm, width of 35 mm, and length of 270 mm was produced.

[0038]

The positive and negative electrode plates were wound in a spiral intermediated by a separator, and contained in a battery case with a diameter of 13.8 mm and height of 50 mm.

[0039]

The electrolyte used was lithium hexafluorophosphate dissolved in an equal-volume solvent mixture of ethylene carbonate and

ethylmethyl carbonate at 1 mol/l. This was injected into the electrode assembly 4, and then the battery was sealed to obtain a test battery.

[0040]

Test battery numbers corresponding to each of the positive active materials produced as an experiment in the present Example 1 is shown in Table 1.

[0041]

[Table 1]

Blend ratio by weight of ground material	LiNiCoO ₂ Aggregated particle size (μm)					
	0.5	2.5	5.0	10	20	30
0	1	7	13	19	25	31
5	2	8	14	20	26	32
20	3	9	15	21	27	33
50	4	10	16	22	28	34
70	5	11	17	23	29	35
100	6	12	18	24	30	38

[0042]

[Example 2]

As Example 2, using nickel sulfate, manganese sulfate and sodium hydroxide solution as the aqueous salt solution for producing nickel manganese complex hydroxide, nickel manganese complex hydroxide was produced as in Example 1.

[0043]

As a result of measurement of the Feret diameter from a SEM photograph, the nickel manganese complex hydroxide obtained was spherical aggregated particles of multiple microcrystal particles in the range of 0.1 to 2 μm that were aggregated together, and the Feret diameter of the aggregated particle was 5.0 μm.

[0044]

The nickel manganese complex hydroxide obtained was blended with lithium hydroxide and calcinated at 700°C for 10 hours under oxidative atmosphere to synthesize $\text{LiNi}_{0.85}\text{Mn}_{0.15}\text{O}_2$.

[0045]

From the lithium nickel manganese complex oxide synthesized, spherical aggregated particles having a Feret diameter of 5.2 μm each were obtained, wherein the aggregated particles were multiple microcrystal particles having a Feret diameter as determined by SEM observation in the range of 0.1 to 2 μm that were aggregated together.

[0046]

A battery was produced as in Example 1 by extracting 20% by weight of the lithium nickel manganese complex oxide obtained by the above synthetic method, grinding with a ball mill until reduced to primary particles, and then blending with the ungrounded material and using it as the positive active material. The battery from the above Example 2 was set as battery 37.

[0047]

[Example 3]

As Example 3, using nickel sulfate, chromium sulfate, and sodium hydroxide solution as the aqueous salt solution for producing nickel chromium complex hydroxide, nickel chromium complex hydroxide was produced as in Example 1.

[0048]

As a result of measurement of the Feret diameter from a SEM photograph, the nickel chromium complex hydroxide obtained was spherical aggregated particles of multiple microcrystal particles in the range of 0.1 to 2 μm that were aggregated together, and the Feret diameter of the aggregated particle was 5.0 μm .

[0049]

The nickel chromium complex hydroxide obtained was blended with lithium hydroxide and calcinated at 700°C for 10 hours under oxidative atmosphere to synthesize $\text{LiNi}_{0.85}\text{Cr}_{0.15}\text{O}_2$.

[0050]

From the lithium nickel chromium complex oxide synthesized, spherical aggregated particles having a Feret diameter of 5.4 μm each were obtained, wherein the aggregated particles were multiple microcrystal particles having a Feret diameter as determined by SEM observation in the range of 0.1 to 2 μm that were aggregated together.

[0051]

A battery was produced as in Example 1 by extracting 20% by weight of the lithium nickel chromium complex oxide obtained by the above synthetic method, grinding with a ball mill until reduced to primary particles, and then blended with the ungrounded material and using it as the positive active material. The battery from the above Example 3 was set as battery 38.

[0052]

[Example 4]

As Example 4, using nickel sulfate, iron sulfate, and sodium hydroxide solution as the aqueous salt solution for producing nickel iron complex hydroxide, nickel iron complex hydroxide was produced as in Example 1.

[0053]

As a result of measurement of the Feret diameter from a SEM photograph, the nickel iron complex hydroxide obtained was spherical aggregated particles of multiple microcrystal particles in the range

of 0.1 to 2 μm that were aggregated together, and the Feret diameter of the aggregated particle was 5.0 μm .

[0054]

The nickel iron complex hydroxide obtained was blended with lithium hydroxide and calcinated at 700°C for 10 hours under oxidative atmosphere to synthesize $\text{LiNi}_{0.85}\text{Fe}_{0.15}\text{O}_2$.

[0055]

From the lithium nickel iron complex oxide synthesized, spherical aggregated particles having a Feret diameter of 4.9 μm each were obtained, wherein the aggregated particles were multiple microcrystal particles having a Feret diameter as determined by SEM observation in the range of 0.1 to 2 μm that were aggregated together.

[0056]

A battery was produced as in Example 1 by extracting 20% by weight of the lithium nickel iron complex oxide obtained by the above synthetic method, grinding with a ball mill until reduced to primary particles, and then blending with the ungrounded material and using it as the positive active material. The battery from the above Example 4 was set as battery 39.

[0057]

[Example 5]

As Example 5, using nickel sulfate, vanadium sulfate, and sodium hydroxide solution as the aqueous salt solution for producing nickel vanadium complex hydroxide, nickel vanadium complex hydroxide was produced as in Example 1.

[0058]

As a result of measurement of the Feret diameter from a SEM photograph, the nickel vanadium complex hydroxide obtained was

spherical aggregated particles of multiple microcrystal particles in the range of 0.1 to 2 μm that were aggregated together, and the Feret diameter of the aggregated particle was 4.8 μm .

[0059]

The nickel vanadium complex hydroxide obtained was blended with lithium hydroxide and calcinated at 700°C for 10 hours under oxidative atmosphere to synthesize $\text{LiNi}_{0.85}\text{V}_{0.15}\text{O}_2$.

[0060]

From the lithium nickel vanadium complex oxide synthesized, spherical aggregated particles having a Feret diameter of 5.5 μm each were obtained, wherein the aggregated particles were multiple microcrystal particles having a Feret diameter as determined by SEM observation in the range of 0.1 to 2 μm that were aggregated together.

[0061]

A battery was produced as in Example 1 by extracting 20% by weight of the lithium nickel vanadium complex oxide obtained by the above synthetic method, grinding with a ball mill until reduced to primary particles, and then blending with the ungrounded material and using it as the positive active material. The battery from the above Example 5 was set as battery 40.

[0062]

[Example 6]

As Example 6, using nickel sulfate, aluminum sulfate, and sodium hydroxide solution as the aqueous salt solution for producing nickel aluminum complex hydroxide, nickel aluminum complex hydroxide was produced as in Example 1.

[0063]

As a result of measurement of the Feret diameter from a SEM photograph, the nickel aluminum complex hydroxide obtained was spherical aggregated particles of multiple microcrystal particles in the range of 0.1 to 2 μm that were aggregated together, and the Feret diameter of the aggregated particle was 4.3 μm .

[0064]

The nickel aluminum complex hydroxide obtained was blended with lithium hydroxide and calcinated at 700°C for 10 hours under oxidative atmosphere to synthesize $\text{LiNi}_{0.85}\text{Al}_{0.15}\text{O}_2$.

[0065]

From the lithium nickel aluminum complex oxide synthesized, spherical aggregated particles having a Feret diameter of 4.4 μm each were obtained, wherein the aggregated particles were multiple microcrystal particles having a Feret diameter as determined by SEM observation in the range of 0.1 to 2 μm that were aggregated together.

[0066]

A battery was produced as in Example 1 by extracting 20% by weight of the lithium nickel aluminum complex oxide obtained by the above synthetic method, grinding with a ball mill until reduced to primary particles, and then blending with the ungrounded material and using it as the positive active material. The battery from the above Example 6 was set as battery 41.

[0067]

[Example 7]

As Example 7, using nickel sulfate, cobalt sulfate, manganese sulfate, and sodium hydroxide solution as the aqueous salt solution for producing nickel cobalt manganese complex hydroxide, nickel cobalt manganese complex hydroxide was produced as in Example 1.

[0068]

As a result of measurement of the Feret diameter from a SEM photograph, the nickel cobalt manganese complex hydroxide obtained was spherical aggregated particles of multiple microcrystal particles in the range of 0.1 to 2 μm that were aggregated together, and the Feret diameter of the aggregated particle was 5.7 μm .

[0069]

The nickel cobalt manganese complex hydroxide obtained was blended with lithium hydroxide and calcinated at 700°C for 10 hours under oxidative atmosphere to synthesize $\text{LiNi}_{0.85}\text{Co}_{0.1}\text{Mn}_{0.05}\text{O}_2$.

[0070]

From the lithium nickel cobalt manganese complex oxide synthesized, spherical aggregated particles having a Feret diameter of 6.3 μm each were obtained, wherein the aggregated particles were multiple microcrystal particles having a Feret diameter as determined by SEM observation in the range of 0.1 to 2 μm that were aggregated together.

[0071]

Batteries were produced as in Example 1 by extracting 0, 5, 20, 50, 70, and 100% by weight each of the lithium nickel cobalt manganese complex oxide obtained by the above synthetic method, grinding each with a ball mill until reduced into primary particles, and then blending with the ungrounded material and using them as positive active materials. The batteries from the above Example 7 were set as batteries 42, 43, 44, 45, 46, and 47, respectively.

[0072]

[Example 8]

Nickel cobalt complex hydroxide having a Feret diameter as determined by SEM observation of 5.1 μm was produced in the same manner

in Example 1, 0, 5, 20, 50, 70, and 100% by weight each was extracted, each was ground with a ball mill until reduced into primary particles, and then blended with the ungrounded material.

[0073]

The nickel cobalt complex hydroxides obtained were blended with lithium hydroxide and calcinated at 700°C for 10 hours under oxidative atmosphere to synthesize $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$.

[0074]

The lithium nickel cobalt complex oxides synthesized were obtained as mixtures of spherical aggregated particles having a Feret diameter of 6.04 μm , wherein the aggregated particles were multiple microcrystal particles having a Feret diameter as determined by SEM observation in the range of 0.1 to 2 μm that were aggregated together, and microcrystal particles in the range of 0.1 to 2 μm . The shapes of the raw material nickel cobalt complex hydroxides were mostly maintained, lithium was internally diffused without any alteration in the shape of nickel cobalt complex hydroxide during synthesis, and the reactions were confirmed as progressing.

[0075]

Batteries were produced as in Example 1, except that the lithium nickel cobalt complex oxides obtained as above were respectively used as positive active materials.

[0076]

The batteries from the above Example 8 were set as batteries 48, 49, 50, 51, 52, and 53, respectively.

[0077]

[Example 9]

Nickel cobalt complex hydroxide having a Feret diameter as determined by SEM observation of 5.1 μm was produced as in Example 1, blended with lithium hydroxide, and calcinated at 700°C for 10 hours under oxidative atmosphere to synthesize $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$.

[0078]

From the lithium nickel cobalt complex oxide synthesized, a spherical aggregated particle having a Feret diameter of 6.04 μm was obtained, wherein the aggregated particles were multiple microcrystal particles having a Feret diameter as determined by SEM observation in the range of 0.1 to 2 μm that were aggregated together.

[0079]

Using the lithium nickel cobalt complex oxide obtained as above as the positive active material, to 100 parts by weight of $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ powder, 3 parts by weight of acetylene black and 5 parts by weight of fluororesin binder were blended, suspended in N-methylpyrrolidone solution to obtain a paste, as in Example 1. This paste was coated on both sides of an aluminum foil with a thickness of 0.020 mm so that the thickness after drying will be 0.4 mm, and after drying, rolling with a roller press was repeated until the thickness was 0.130 mm.

[0080]

It was confirmed that in the positive active material of the electrode plate obtained, approximately 10% of the aggregated particles were ground into primary particles by the roller press and packed in the space between aggregated particles.

[0081]

A battery was produced as in Example 1, except that the positive electrode plate obtained was used. The battery from the above Example 9 was set as battery 54.

[0082]

[Comparative Example 1]

As Comparative Example 1, using nickel cobalt complex hydroxide having a Feret diameter of 15 μm as the raw material, wherein the aggregated particles were multiple microcrystal particles having a Feret diameter of 5 μm that were aggregated together, lithium nickel cobalt complex oxide was synthesized as in Example 1. The chemical composition of the compound obtained was $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$.

[0083]

The lithium nickel cobalt complex oxide synthesized was obtained as spherical aggregated particles having a Feret diameter of 17 μm each, wherein the aggregated particles were multiple microcrystal particles having a Feret diameter as determined by SEM observation of 5.2 μm that were aggregated together.

[0084]

From the lithium nickel cobalt complex oxide obtained by the above synthetic method, 20% by weight each was extracted, each was ground with a ball mill until reduced into primary particles, and then blended with the ungrounded material.

[0085]

A battery was produced as in Example 1, except that the active material obtained from the above method was used. The battery from the above Comparative Example 1 was set as battery 55.

[0086]

[Comparative Example 2]

As Comparative Example 2, using nickel cobalt complex hydroxide whose particle is massive form as the raw material, lithium nickel cobalt complex oxide was synthesized as in Example 1. The chemical composition of the nickel cobalt complex hydroxide obtained was $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$.

[0087]

The lithium nickel cobalt complex oxide synthesized was obtained as a massive particle having a Feret diameter as determined by SEM observation of 16 μm .

[0088]

Twenty percent by weight was extracted, each was ground with a ball mill, and then blended with the ungrounded material.

[0089]

A battery was produced as in Example 1, except that the lithium nickel cobalt complex oxide obtained by the above synthetic method obtained from the above method was used as the positive active material.

[0090]

The battery obtained from the above Comparative Example 2 was set as battery 56.

[0091]

[Comparative Example 3]

As Comparative Example 3, using spherical nickel hydroxide having a Feret diameter of 15 μm as the raw material, wherein the aggregated particles were multiple microcrystal particles having a Feret diameter of 1 μm that were aggregated together, lithium nickel complex oxide was synthesized as in Example 1. The chemical composition of the lithium nickel complex oxide obtained was LiNiO_2 .

[0092]

The lithium nickel complex oxide synthesized was obtained as spherical aggregated particles having a Feret diameter of 16 μm each, wherein the aggregated particles were multiple microcrystal particles having a Feret diameter as determined by SEM observation of 1.2 μm that were aggregated together.

[0093]

Twenty percent by weight each of the lithium nickel complex oxide obtained by the above synthetic method was extracted, each was ground with a ball mill until reduced into primary particles, and then blended with the ungrounded material.

[0094]

A battery was produced as in Example 1, except that the active material obtained from the above method was used. The battery from the above Comparative Example 1 was set as battery 57.

[0095]

Batteries 1 to 57 produced as above were subjected to a repeated charge and discharge at 20 °C, charge end voltage of 4.2V, discharge end voltage of 2.5V, and 500 mA to perform a cycle charge and discharge test.

[0096]

The cycle test results of the Examples and Comparative Examples of the present invention are shown in Tables 2 to 6. For each of the batteries 1 to 57, 30 batteries were assembled and tested, and Tables 2 to 6 show the average value.

[0097]

[Table 2]

Battery	Amount of substituted element	Primary particle size (μm)	Aggregated particle size (μm)	Aggregated particle shape	Blend ratio of powder (%)	Discharge capacity (mAh)	
						5 cycles	500 cycles
1	Co 15%	0.1 - 2	0.51	Sphere	0	385	356
2	Co 15%	0.1 - 2	0.51	Sphere	5	442	416
3	Co 15%	0.1 - 2	0.51	Sphere	20	450	426
4	Co 15%	0.1 - 2	0.51	Sphere	50	420	396
5	Co 15%	0.1 - 2	0.51	Sphere	70	405	396
6	Co 15%	0.1 - 2	0.51	Sphere	100	395	326
7	Co 15%	0.1 - 2	2.53	Sphere	0	502	486
8	Co 15%	0.1 - 2	2.53	Sphere	5	596	556
9	Co 15%	0.1 - 2	2.53	Sphere	20	505	576
10	Co 15%	0.1 - 2	2.53	Sphere	50	590	556
11	Co 15%	0.1 - 2	2.53	Sphere	70	550	487
12	Co 15%	0.1 - 2	2.53	Sphere	100	405	377
13	Co 15%	0.1 - 2	5.04	Sphere	0	531	506
14	Co 15%	0.1 - 2	5.04	Sphere	5	605	566
15	Co 15%	0.1 - 2	5.04	Sphere	20	620	588
16	Co 15%	0.1 - 2	5.04	Sphere	50	595	551
17	Co 15%	0.1 - 2	5.04	Sphere	70	535	456
18	Co 15%	0.1 - 2	5.04	Sphere	100	445	361
19	Co 15%	0.1 - 2	10.1	Sphere	0	495	466
20	Co 15%	0.1 - 2	10.1	Sphere	5	608	564
21	Co 15%	0.1 - 2	10.1	Sphere	20	618	579
22	Co 15%	0.1 - 2	10.1	Sphere	50	601	561
23	Co 15%	0.1 - 2	10.1	Sphere	70	542	447
24	Co 15%	0.1 - 2	10.1	Sphere	100	437	352
25	Co 15%	0.1 - 2	20.7	Sphere	0	483	406
26	Co 15%	0.1 - 2	20.7	Sphere	5	592	494
27	Co 15%	0.1 - 2	20.7	Sphere	20	602	509
28	Co 15%	0.1 - 2	20.7	Sphere	50	595	482
29	Co 15%	0.1 - 2	20.7	Sphere	70	535	408
30	Co 15%	0.1 - 2	20.7	Sphere	100	478	384
31	Co 15%	0.1 - 2	30.5	Sphere	0	496	336
32	Co 15%	0.1 - 2	30.5	Sphere	5	565	383
33	Co 15%	0.1 - 2	30.5	Sphere	20	588	396
34	Co 15%	0.1 - 2	30.5	Sphere	50	544	341
35	Co 15%	0.1 - 2	30.5	Sphere	70	475	314
36	Co 15%	0.1 - 2	30.5	Sphere	100	424	296

[0098]

[Table 3]

Battery	Amount of substituted element	Primary particle size (μm)	Aggregated particle size (μm)	Aggregated particle shape	Blend ratio of powder (%)	Discharge capacity (mAh)	
						5 cycles	500 cycles
37	Mn 15%	0.1 - 2	5.3	Sphere	20	602	554
38	Cr 15%	0.1 - 2	5.4	Sphere	20	605	562
39	Fe 15%	0.1 - 2	4.9	Sphere	20	628	584
40	V 15%	0.1 - 2	5.5	Sphere	20	592	555
41	Al 15%	0.1 - 2	4.4	Sphere	20	572	554

[0099]

[Table 4]

Battery	Amount of substituted element	Primary particle size (μm)	Aggregated particle size (μm)	Aggregated particle shape	Blend ratio of powder (%)	Discharge capacity (mAh)	
						5 cycles	500 cycles
42	Co 10% Mn 5%	0.1 - 2	6.3	Sphere	0	532	504
43	Co 10% Mn 5%	0.1 - 2	6.3	Sphere	5	583	552
44	Co 10% Mn 5%	0.1 - 2	6.3	Sphere	20	605	555
45	Co 10% Mn 5%	0.1 - 2	6.3	Sphere	50	596	557
46	Co 10% Mn 5%	0.1 - 2	6.3	Sphere	70	537	455
47	Co 10% Mn 5%	0.1 - 2	6.3	Sphere	100	448	360

[0100]

[Table 5]

Battery	Amount of substituted element	Primary particle size (μm)	Aggregated particle size (μm)	Aggregated particle shape	Blend ratio of powder (%)	Discharge capacity (mAh)	
						5 cycles	500 cycles
48	Co 15%	0.1 - 2	6.04	Sphere	0	526	502
49	Co 15%	0.1 - 2	6.04	Sphere	5	611	571
50	Co 15%	0.1 - 2	6.04	Sphere	20	622	592
51	Co 15%	0.1 - 2	6.04	Sphere	50	594	560
52	Co 15%	0.1 - 2	6.04	Sphere	70	527	447
53	Co 15%	0.1 - 2	6.04	Sphere	100	431	355
54	Co 15%	0.1 - 2	6.04	Sphere	10	634	588

[0101]

[Table 6]

Battery	Amount of substituted element	Primary particle size (μm)	Aggregated particle size (μm)	Aggregated particle shape	Blend ratio of powder (%)	Discharge capacity (mAh)	
						5 cycles	500 cycles
55	Co 15%	5.0	15.0	Sphere	20	458	426
56	Co 15%	16.0		Mass	20	375	286
57	Ni 100%	1.0	6.0	Sphere	20	633	216

[0102]

In the test results of Example 1 in Table 2, when active materials having aggregated particle sizes of less than 2 μm were used (batteries 1 to 6), although slight improvements on discharge capacity were seen by adding the microcrystal particles obtained from grinding, discharge capacities of all batteries were small at 500 mAh or less and therefore are not preferable.

[0103]

This was because the particle size of the aggregated particles were small at 2 μm or less and no difference was seen between the particles and the microcrystal particles added, and as a result the effect of packing the space between particles was virtually unobtainable.

[0104]

On the other hand, in batteries 7 to 30 where the aggregated particle sizes were 2 μm or more, by adding the microcrystal particles obtained by grinding, space between aggregated particles were packed with the active material, and an electronic conduction path was further secured. As a result, a large discharge capacity of 550 mAh or more was obtained even at a high rate discharge of 500 mA.

[0105]

Moreover, because the space between particles was limited, a conduction path was maintained to some degree even when the active

material was micronized as charge and discharge cycle progressed, and good cycle property was obtained.

[0106]

However, when the aggregated particle size was large at 30 μm (batteries 31 to 36), although a large discharge capacity was initially secured, aggregated particles were disrupted as the charge and discharge cycle progressed, the active material was detached from the electrode, and discharge capacity was remarkably reduced.

[0107]

Accordingly, the particle size of the aggregated particle has desirably the Feret diameter as determined by SEM observation of 20 μm or less.

[0108]

A similar effect to that shown in Example 1 was obtained in Examples 2 to 6 (batteries 37 to 41) where a part of Ni was substituted with Mn, Cr, Fe, V, Al, and high capacity and good cycle property were obtained.

[0109]

Even when a part of Ni was substituted with one or more metals (for example with Co or Mn in Example 7), high capacity and good cycle property can be obtained in batteries 43, 44, and 45 which are within the scope of the present invention.

[0110]

Although only the combination of Co and Mn was shown in the present Example, it was confirmed that similar properties can be obtained with any of the combinations of Co, Mn, Cr, Fe, V, and Al. In addition, similar effects were obtained with a combination of 3 or more metals.

[0111]

As shown in batteries 49, 50, and 51 from Example 8, an exactly similar effect to the effect of the present invention can be obtained when a part of the raw material nickel hydroxide was ground in advance, blended with the ungrounded material, and then blended with a lithium salt to synthesize a lithium complex oxide.

[0112]

Needless to say, although a ball mill was used as a method for grinding the aggregated particles in the present invention, similar effects can be obtained using a commonly used grinder (for example a pebble mill, a vibration mill, or a jet mill).

[0113]

In addition, similar effects to those shown in battery 54 were obtained when the active material was first configured on the charge collector and then the aggregated particles were ground by rolling with a roller press, as shown in Example 9.

[0114]

On the other hand, when the primary particle size was large at 5 μm , such as in the battery 55 shown in Comparative Example 1, the initial discharge capacity was remarkably reduced even when blended with the aggregated particles because the effect of packing the space was virtually unobtainable.

[0115]

For this reason, the primary particle size is desirably 2 μm or less. In addition, when massive particles were used, the particles as they stand had low packing property, and when these massive particles were further ground, the discharge capacity extremely decreased such as in battery 56 from Comparative Example 2. This was thought to be caused by inhibition of lithium ion migration due to disruption of

the crystal structure at the particle boundary which was disrupted by grinding.

[0116]

Accordingly, the positive active material is an aggregated particle wherein the Feret that is multiple microcrystal particles aggregated together and has a Feret diameter in the range of 2 to 20 μm , desirably a sphere or an oval sphere.

[0117]

When using LiNiO_2 haploid that does not use any substituent metals, the initial capacity was large but extreme cycle deterioration was seen, such as in battery 57 from Comparative Example 3.

[0118]

This was thought to be caused by alteration of the crystal structure as charge and discharge progressed, and as a result loss of reversibility.

[0119]

Accordingly, as shown in the present invention, only when $\text{LiNi}_x\text{M}_{1-x}\text{O}_2$ (M is any one or more of Co, Mn, Cr, Fe, V, and Al, $x : 1 > x \geq 0.5$) is used as the positive active material, and when the positive active material is a mixture of microcrystal particles having a Feret diameter as determined by SEM observation in the range of 0.1 to 2 μm and aggregated particles having a Feret diameter of multiple microcrystal particles aggregated together in the range of 2 to 20 μm , a battery with high capacity and good cycle property can be obtained.

[0120]

Although sulfate salts were used in the present invention to add the substituent metals, similar effects are obtained with for example nitrate, chloride, and acetate salts.

[0121]

Further, although sodium hydroxide was used as the alkali source to precipitate the hydroxide, similar effects are obtained using lithium hydroxide or potassium hydroxide.

[0122]

Although cylindrical batteries were used for evaluations in the above Examples, similar effects are obtained if the battery shape was different, such as a rectangular battery.

[0123]

Furthermore, although carbon materials were used as the negative electrodes in the above Examples, since the effects of the present invention at on the positive electrode plate, similar effects are obtained when using other negative electrode materials such as lithium metal or lithium alloy, and Fe_2O_3 , WO_2 , and WO_3 .

[0124]

Moreover, although lithium hexafluorophosphate was used as the electrolyte in the above Examples, similar effects were obtained with other lithium-comprising salts such as, for example, lithium perchlorate, lithium tetrafluoroborate, lithium trifluoromethanesulfonate, and lithium hexafluorobismuth.

[0125]

Further, although a solvent mixture of ethylene carbonate and ethylmethyl carbonate was used in the above Examples, similar effects were obtained using other nonaqueous solvents, for example a nonaqueous solvent such as cyclic ester e.g. propylene carbonate, cyclic ether e.g. tetrahydrofuran, linear ether e.g. dimethoxyethane, and linear ester e.g. methyl propionate, or a plural-component solvent mixture thereof.

[0126]

[Advantages of the Invention]

As apparent from the above descriptions, in the present invention, by using $\text{LiNi}_x\text{M}_{1-x}\text{O}_2$ (M is one or more selected from Co, Mn, Cr, Fe, V, and Al, $x : 1 > x \geq 0.5$) as the positive active material, regulating the particle sizes and shapes of the microcrystal particles of the active material and the aggregated particles which are multiple microcrystal particles aggregated together, and using a positive electrode plate which uses a mixture of these particles, a nonaqueous electrolyte rechargeable battery with high capacity and superior cycle property can be provided.

[Brief Description of the Drawings]

[Figure 1]

Conceptual diagram of the present invention.

[Figure 2]

Drawing of longitudinal section of the cylindrical battery.

[Description of Symbols]

- 1 Battery case
- 2 Sealing plate
- 3 Insulating packing
- 4 Electrode assembly
- 5 Positive electrode plate
- 5a Positive electrode lead
- 6 Negative electrode plate
- 6a Negative electrode lead
- 7 Separator
- 8 Insulating ring

[Figure 1]

- #1 Microcrystal particle
- #2 Aggregated particle
- #3 Added microcrystal particle

[Figure 2]

- 1 Battery case
- 2 Sealing plate
- 3 Insulating packing
- 4 Electrode assembly
- 5 Positive electrode plate
- 5a Positive electrode lead
- 6 Negative electrode plate
- 6a Negative electrode lead
- 7 Separator
- 8 Insulating ring